able to obtain saline compounds with hydrochloric and sulphuric acid. It forms, however, compounds with nitrate of silver and bichloride of platinum. The latter has the usual composition, viz.—

$$C_{14} H_8 N_2 S_2, H Cl, Pt Cl_2.$$

Boiled with nitrate of silver, the new compound loses its sulphur, which is replaced by oxygen, phenylcarbamide, $C_{14} H_8 N_2 O_2$, being produced, a substance which I described many years ago. Sulphocyanide of phenyl is acted upon by a great number of ammonias with formation of bodies the composition of which is sufficiently pointed out by theory.

The mode of producing cyanate and sulphocyanide of phenyl, which I have described in the preceding paragraphs, deserves some notice, since the usual processes suggested by the experience in the methyl-, ethyl- and amyl-series, such as distillation of sulphophenylates with cyanates and sulphocyanides, have altogether failed in producing the desired result. The same reaction may be of course applied to tolylamine, cumylamine, naphthylamine, and all primary monamines.

IV. "Notes of Researches on the Poly-Ammonias."—No. IV. Action of Bibromide of Ethylene upon Aniline. By A. W. Hofmann, Ph.D., F.R.S. &c. Received May 13, 1858.

While engaged in some experiments on the action of bibromide of ethylene on ammonia, a short account of which I have lately communicated to the Royal Society*, I induced Mr. Henry Bassett, then working in my laboratory, to study the deportment of the same bromide with aniline, a characteristic representative of the class of primary monamines. In the following pages I propose to submit to the Society Mr. Bassett's observations, together with the results of a series of experiments which I carried out myself after Mr. Bassett by circumstances had been prevented from a further continuation of the inquiry.

A mixture of 1 volume of the bibromide of ethylene and 2 volumes

* Proceedings of the Royal Society, vol. ix. page 150.

of aniline, when exposed to the temperature of boiling water for an hour or two, solidifies into a crystalline mass of more or less solidity. This mass is chiefly hydrobromate of aniline; it contains, however, in addition, three new organic bases, partly free, partly in the form of hydrobromates. These substances are formed in very different quantities,—a beautiful crystalline body, difficultly soluble in alcohol, being invariably the chief product of the reaction, while the two other bases, the one solid but extremely soluble in alcohol, the other likewise solid but quite insoluble in this liquid, are found to be present in much smaller proportions.

The preparation, in a state of purity, of the principal product of the reaction presents no difficulty. The solid mass obtained by digesting bibromide of ethylene and aniline in the stated proportions is mixed with water, and submitted to distillation, when any bibromide left unchanged, together with some unaltered aniline, passes over. The residuary liquid is then mixed with a strong solution of potassa, which separates all the bases existing as hydrobromates in the form of a semi-solid resin. This is washed with water and then again submitted to distillation with water, when, together with more or less water, an additional quantity of aniline distils. The residuary mass, when treated with boiling (methylated) spirit, leaves the insoluble base as a white, flour-like powder, while the other two bases dissolve. On cooling, the solution deposits a beautiful crystallization of white needles, while the more soluble base remains dissolved in the spirit. The crystals are rather difficultly soluble in alcohol; two or three crystallizations from this solvent render them absolutely pure.

Thus obtained, the new base, for which, in accordance with the results of analysis, I propose the name *ethylene-phenylamine*, is a snow-white, inodorous and tasteless crystalline compound, of nacreous lustre, insoluble in water, soluble in boiling, less so in cold alcohol, soluble in ether. The solutions are without action on vegetable colours. The substance dissolves readily in hydrochloric, sulphuric and nitric acids, especially on gently heating the liquids, which on cooling deposit well crystallized saline compounds. The hydrochlorate yields yellow precipitates with bichloride of platinum and terchloride of gold. When exposed to the action of heat, ethylene-phenylamine fuses at 148° C.; at a temperature approaching 300° it begins to boil

and to distil, the larger portion undergoing decomposition. Among the products of decomposition which are not yet sufficiently examined, considerable quantities of aniline make their appearance. The results obtained in the analysis of ethylene-phenylamine lead to the formula

$$C_{16}H_9N$$

as the simplest molecular expression for this compound.

This formula is confirmed by the analysis of the hydrochlorate and of the platinum-salt, the preparation of which, on account of their instability, requires some management.

These salts contain respectively

Hydrochlorate.....$C_{16}H_9N$, HCl.
Platinum-salt .....$C_{16}H_9N$, HCl, $PtCl_2$.

The reaction which gives rise to ethylene-phenylamine is expressed by the following equation:—

$$\underbrace{2C_{12}H_7N}_{\text{Phenylamine.}} + \underbrace{C_4H_4Br_2}_{\text{Bibromide of ethylene.}} = \underbrace{C_{12}H_7N, HBr}_{\text{Hydrobromate of phenylamine.}} + \underbrace{C_{16}H_9N, HBr}_{\text{Hydrobromate of ethylene-phenylamine.}}.$$

What is the constitution of this new base? This question could not be answered without further experiments, on account of the twofold nature of bibromide of ethylene. In many cases this remarkable compound exhibits the character of the hydrobromic ether of a biacid ethylene-alcohol, of $(C_4H_4)''Br_2$, whilst in the majority of reactions it splits into hydrobromic acid and the bromide C_4H_3Br, which might be considered as the hydrobromic ether of a monacid alcohol, $C_4H_4O_2$, homologous to allylic alcohol. It remained therefore uncertain whether the new basic compound retained the original molecule $(C_4H_4)''$ replacing 2 equivs. of hydrogen, or the modified molecule C_4H_3 replacing 1 equiv. of hydrogen. In other words, it had to be established by further experiments, whether the base was

$$\left.\begin{matrix}(C_4\ H_4)''\\ C_{12}\ H_5\end{matrix}\right\} N = C_{16}H_9N, \text{ or}$$

$$\left.\begin{matrix}C_4\ H_3\\ C_{12}\ H_5\\ H\end{matrix}\right\} N = C_{16}H_9N.$$

The deportment of the substance with iodide of methyl and ethyl, which immediately will be mentioned somewhat more in detail, has

decided in favour of the former view, and in accordance with it the name of the substance has been selected.

It deserves to be noticed, that there are already two other bases known which have exactly the same composition, the one obtained by M. Natanson in the reaction of bichloride of ethylene upon aniline, and described by him as *acetylaniline*, the other discovered by M. Dusart among the derivatives of nitronaphtaline and designated as phtalidine. It is only necessary superficially to glance at the description of these bodies in order to see that they are essentially different from ethylene-phenylamine. The constitution of acetylaniline and phtalidine has not been experimentally fixed. It is probable that Natanson's base contains the molecule $C_4 H_3$ formerly called acetyl, but for which the more appropriate term vinyl has lately been proposed, while phtalidine probably derives from the hydrocarbon styrol or an isomeric body, so that the difference in the constitution of the three bodies would be expressed in the following formulæ:—

Phtalidine Styrylamine (?)	$\left\{\begin{matrix} C_{16} H_7 \\ H \\ H \end{matrix}\right\}$	N.
Acetylaniline Vinyl-phenylamine	$\left\{\begin{matrix} C_4 H_3 \\ C_{12} H_5 \\ H \end{matrix}\right\}$	N.
Ethylene-phenyl-amine	$\left\{\begin{matrix} (C_4 H_4)'' \\ C_{12} H_5 \end{matrix}\right\}$	N.

I have already mentioned that the degree of substitution of ethylene-phenylamine was fixed by the deportment of this base with iodide of methyl and ethyl, bibromide of ethylene exerting no longer any influence upon it, even by protracted contact, at temperatures varying from 100° to 150° C.

A mixture of ethylene-phenylamine and iodide of methyl, on the other hand, when exposed for some hours to the temperature of boiling water, solidifies to a resinous mass, floating, together with a portion of unchanged base, in the excess of the iodide. Distillation with water separates the excess of iodide of methyl; and washing with cold water until the filtrate is no longer precipitated by an alkali removes any hydriodate of ethylene-phenylamine formed during the distillation. Lastly, by repeated crystallization of the resinous residue from boiling water, to which a small quantity of spirit may be added in the later stages (separation from ethylene-phenylamine), a perfectly cry-

stalline, slightly yellowish iodine-compound is obtained, which may be dried without decomposition at 100°.

On analysis, this iodine-compound was found to have the remarkable composition

$$C_{34}H_{21}N_2I = \left.\begin{matrix}C_{16}H_9N\\C_{16}H_9N\end{matrix}\right\} C_2H_3I.$$

Treated with oxide of silver, the solution of the iodide yields a powerfully alkaline liquid, possessing all the characters of the class of bodies of which hydrated oxide of tetrethylammonium is the type. On adding hydrochloric acid and bichloride of platinum, this liquid furnishes a pale yellow amorphous platinum-salt containing

$$C_{34}H_{21}N_2Cl,\ PtCl_2 = \left.\begin{matrix}C_{16}H_9N\\C_{16}H_9N\end{matrix}\right\} C_2H_3Cl,\ PtCl_2.$$

A repetition of this experiment in the ethyl-series has given perfectly similar results. On account of the less powerful action of iodide of ethyl, the reaction requires longer digestion. The iodide formed is less soluble in boiling water than the corresponding methyl-compound, and therefore more difficult to separate from any ethylene-phenylamine which may have remained unchanged. When pure, the new iodide is a yellowish white substance crystallizing in needles. It fuses in the water-bath without decomposition to a yellow oil, which solidifies on cooling into a brittle crystalline mass.

On analysis, numbers were obtained corroborating in every respect the results furnished by the methyl-series. The iodide contains

$$C_{36}H_{23}N_2I = \left.\begin{matrix}C_{16}H_9N\\C_{16}H_9N\end{matrix}\right\} C_4H_5I.$$

Like the methyl-compound, it is readily decomposed by oxide of silver; and the powerfully alkaline solution yields, with hydrochloric acid and bichloride of platinum, a salt of exactly the same appearance as the salt of the methyl-series. This platinum-salt was found to contain

$$C_{36}H_{23}N_2Cl,\ PtCl_2 = \left.\begin{matrix}C_{16}H_9N\\C_{16}H_9N\end{matrix}\right\} C_4H_5Cl,\ PtCl_2.$$

The action of iodide of methyl and ethyl upon ethylene-phenylamine, although different from what might have been anticipated, nevertheless appears to fix in an unequivocal manner the state of substitution of this base. It is obvious that ethylene-phenylamine no longer contains any replaceable hydrogen, and consequently that the

molecule $(C_4 H_4)''$, equivalent to H_2 as such, has been assimilated by the aniline.

But how is the composition of the bodies formed by the action of iodide of methyl and ethyl to be interpreted? Are they simply compounds of the alcohol-iodides with 2 equivalents of ethylene-phenylamine, analogous to the salts produced by the union of 1 equiv. iodide of mercury with 2 equivs. of ammonia?

Does not the existence of these bodies involve a further consideration of the formula which has been assigned to ethylene-phenylamine? Does the formula $C_{16} H_9 N$ actually represent the molecule of this body, or is it not more correct to double that expression and to consider the formula $C_{32} H_{18} N_2$ as a more appropriate representation of this molecule? Ethylene-phenylamine would then be derived from 2 equivalents of ammonia, it would be a diamine, and the hydrochlorate and the platinum-compounds would appear in the light of diammonium-compounds.

Diethylene-diphenyl-diamine $\left.\begin{matrix}(C_4 H_4)_2'' \\ (C_{12} H_5)_2\end{matrix}\right\} N_2$.

Bichloride..... $\left.\begin{matrix}(C_4 H_4)'' \\ (C_{12} H_5)_2 \\ H_2\end{matrix}\right\} N_2 Cl_2$.

Platinum-salt..... $\left.\begin{matrix}(C_4 H_4)_2'' \\ (C_{12} H_5)_2 \\ H_2\end{matrix}\right\} N_2 Cl_2, 2PtCl_2$.

At the first glance it certainly appears strange that a molecule capable of assimilating 2 equivalents of hydrochloric acid should unite only with 1 equiv. of iodide of methyl or ethyl, well established members of the hydrochloric type. But this deportment after all is not without parallelism.

The expression

$$C_{20} H_{12} NO_2,$$

originally established for quinine by Liebig, supported as it was by the analysis of numerous salts of the formula

$$C_{20} H_{12} NO_2, HX,$$

and especially by that of a platinum-compound,

$$C_{20} H_{12} NO_2, HCl, PtCl_2, aq,$$

was universally adopted by chemists.

A few quinine-salts of the formula

$$2(C_{20}H_{12}NO_2),\ HX$$

were considered as anomalous, as basic compounds; and it was not until the methylic and ethylic derivatives of quinine,

$$2C_{20}H_{12}NO_2,\ C_2H_3I \qquad \text{and}$$
$$2C_{20}H_{12}NO_2,\ C_4H_5I,$$

had been discovered that chemists began to consider the formula

$$C_{40}H_{24}N_2O_4$$

as a more appropriate expression for the molecule of quinine.

Probably further examination of the salts of ethylene-phenylamine —I retain this name for the present—will furnish saline compounds corresponding to the methyl- and ethyl-derivatives, showing that this base, like quinine, is capable of forming two groups of salts.

It deserves to be noticed that the diammonic nature of ethylene-phenylamine is also strongly marked by its deportment under the influence of heat; for while all the monammonic basic derivatives of aniline are volatile without decomposition, ethylene-phenylamine, when submitted to distillation, is destroyed with reproduction of aniline, like the well-established diamines belonging to this group, melaniline, formyl-diphenylamine, &c.

In describing the preparation of ethylene-phenylamine, it has been mentioned that the action of bibromide of ethylene on aniline gives rise at the same time to two other basic compounds. These substances, which are formed in smaller quantity, differ in a very marked manner from the principal product of the reactions. Their study is not yet completed, but it may even now be stated, that they have the same composition as ethylene-phenylamine itself. One of these substances, remarkable for its solubility in spirit, is capable of being converted into ethylene-phenylamine by a simple molecular change. The relation in which these three isomeric bodies stand to each other is not yet finally fixed by experiment. The idea suggests itself that it may possibly be represented by the formulæ—

Soluble base.....	$C_{16}H_9N$.
Ethylene-phenylamine	$C_{32}H_{18}N_2$.
Insoluble base.....	$C_{48}H_{27}N_3$.